

UNPUBLISHED PRELIMINARY DATA

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T Nitric Oxide Photolysis

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OTS; PRICE

XEROX

vs

1.10 ph

MICROFILM

vs

0.80 mf

OTS
(2)

During the past six months the changes made in the procedures outlined in previous reports center mainly in the hydrogen lamp and in the analysis of products. The lamp was modified to include two chambers separated by a large lithium fluoride window to permit the determination of the quantum yields of products at low nitric oxide pressures. The output of the lamp has declined from an initial value of 1.1×10^{16} quanta/sec. to 2.0×10^{15} quanta/sec. This decline has been attributed to a clouding of the lithium fluoride window and not to the gas filling. Frequent determinations of the lamp efficiency preclude any reflection of this change in the values of the quantum yields of photolysis.

Two techniques for the analysis of product gases from the photolysis have been used. These gases include NO, NO₂, N₂O₃, N₂O₄, N₂O and N₂. Between the reaction vessel and pump there are three traps. The first, nearest the reaction vessel, was cooled with liquid nitrogen to -195°C; the second trap, to -210°C with solid nitrogen obtained by pumping on liquid nitrogen and the third trap cooled with liquid nitrogen situated immediately before a Toepler pump. All of the gases with the exception of N₂ were condensed in traps 1 or 2 and the nitrogen was pumped into a vessel of known volume and its pressure measured on an octoil manometer. The condensed gases were vaporized and their total pressure determined. A known volume of oxygen was added to react with the NO present to form NO₂. Frequent condensation and re-evaporation for at least one hour was necessary to insure completion of the oxidation. Residual oxygen was pumped off the frozen gases and its pressure in a known volume measured. From the loss of oxygen, the amount of NO was calculable. When no N₂O was present, the remainder of the sample was taken as NO₂ and N₂O₄. In the analysis for N₂O, the mixture was cooled to -130°C with pentane slush or to -110°C with CS₂ to freeze out N₂O₄. The N₂O could then be pumped off, or frozen into a known volume with liquid nitrogen. This scheme permits a complete analysis of all the products as well as unreacted nitric oxide. The weakest link in the chain is the oxidation of NO, which is very slow at low partial pressures of NO and possibly never quite complete.

A faster technique involved fractionating off the NO first, by removing the liquid and solid nitrogen coolants and cooling traps 2 and 3 with isopentane slush at -160°C. The NO was pumped by the Toepler into a known volume and the pressure measured on the octoil manometer. Nitrous oxide was next removed by warming the traps to -110°C and the amount determined in a similar manner. When NO was present in excess, the residue in the traps was N₂O₃ formed on condensation of NO and NO₂. However, if stoichiometric amounts of NO and NO₂ are condensed, vaporized and recondensed, instead of N₂O₃ being found, N₂O₃, N₂O₄ and NO are found in varying amounts. At -160°C, NO is volatile but NO₂ is solid and a separation is possible. The procedure used earlier of permitting the N₂O₃ condensed in trap 1 to vaporize and be condensed in trap 2 in which most of the excess NO was already condensed led to an error in the quantum yields calculated earlier, that of NO₂ production being low, that of NO decomposed, high, relative to Heat of N₂ produced. This error was eliminated by controlling the trap temperatures to avoid vaporization of N₂O₃.

A problem in the analysis of NO₂ arises from its reaction with mercury vapor. To avoid this, mercury vapor was removed from the system by long pumping through liquid nitrogen and the use of octoil manometer for pressure measurements. The NO₂ measure was obtained as half the total pressure of K₂O₂ fraction when warmed to room temperature. Since the total pressure of the fraction was low (5mmHg) the dissociation of N₂O₃ into NO and NO₂ would be complete. The whole analysis scheme was checked mass-spectrometrically.

Results

a) Hydrogen Discharge. Table I presents results with the earlier lamp used. Only quantum yields of N_2 production are given since NO_2 production and NO decomposition were shown above to be in error due to faulty analytical technique. Later results with the new lamp and new analytical technique are shown in Table II. No concrete evidence for the formation of N_2O was obtained in this spectral region, either from pure NO or when helium, argon or nitrogen was added. The precision of the NO_2 production and NO decomposition yields cannot be as high as that of N_2 production

Table I

Preliminary Photolyses of NO by H_2 Discharge

Run No.	P _{NO} (mmHg)	gas	added gas P (mmHg)	% NO	ϕ_{N_2}
14	55.2				0.415
15	124.4				0.466
4	181.0				0.520
18	181.2				0.511
6	186.2				0.581
19	280.5				0.489
7	285.4				0.590
17	737.9				0.486
16	756.6				0.535
29	812.9				0.542
20	33.8	Ar.	43.5	43.7	0.565

Table II

Photolysis of Nitric Oxide

Hydrogen Discharge; New Lamp

Run No.	Initial NO (mmHg)	added gas	P (mmHg)	ϕ_{N_2}	ϕ_{NO_2}	ϕ_{NO}	ϕ_{NO_2}/ϕ_{N_2}	ϕ_{NO}/ϕ_{N_2}
60	1.539			0.215	0.333	0.812	1.55	3.78
49	4.858			0.268	0.403	1.117	1.50	4.17
56	5.202			0.326	0.666	1.314	2.04	4.03
54	5.389			0.410				
55	5.651			0.333	0.607	1.285	1.82	3.86
57	6.499			0.254	0.310	0.931	1.22	3.67
58	7.278			0.238	0.338	0.958	1.42	4.03
37	10.11			0.399				
64	15.05			0.235	0.312	0.913	1.33	3.89
53	15.61			0.330				
33	22.4			0.326				
59	32.12			0.299	0.420	1.198	1.40	4.01
66	37.60			0.310	0.453	1.311	1.46	4.23
68	38.66			0.273	0.452	1.326	1.66	4.86
63	39.44			0.296	0.501	1.322	1.69	4.47
51	149.0			0.410	0.732		1.79	
45	167.0			0.388		1.786		4.60
86	205.4			0.418	0.851		2.04	
69	341.2			0.412	0.700		1.70	
70	480.2			0.403	0.631		1.57	
39	495.8			0.433	0.735		1.70	
62	6.989	N ₂	184.0		0.336	0.829		
61	7.009	N ₂	195.0		0.331	0.827		
89	167.7	Ar	259.1		0.987	1.422		
91	146.2	He	307.8					

b) Xenon Discharge. The quantum yields obtained using xenon radiation are generally higher than those using the hydrogen lamp. The products are still essentially N₂ and NO₂ but small amounts of N₂O are formed in addition. The determination of this, with precision is difficult. In the fractionation technique the possibility exists that a small amount of N₂O₃ may be measured with the N₂O. Mass-spectrometric analysis too, is uncertain, since when NO₂ is present, oxidation of carbon on the filament yields CO₂ with a mass peak also at 44. The amount of CO₂ must be judged from the 22 mass peak which is not present with N₂O. Resultantly the most reliable estimate of the N₂O quantum yield is about 0.02, far less than the maximum values listed in Table III.

Table III

Photolysis of Nitric Oxide

Xenon Discharge

Run No.	Initial NO (mmHg)	added gas	P (mmHg)	% NO	ϕ_{N_2}	ϕ_{NO_2}	ϕ_{NO}	ϕ_{N_2O} Max.	ϕ_{NO_2}/ϕ_{N_2}	ϕ_{NO}/ϕ_{N_2}
35	10.11				0.353					
82	26.00				0.292	0.624	1.329	0.12	2.11	4.55
78	104.9				0.417	0.839		0.12	2.01	
12	107.3				0.455					
79	119.4				0.415	0.807		0.055	1.94	
80	209.5				0.466	0.913		0.097	1.96	
76	344.2				0.523	1.019	2.709	0.053	1.95	5.18
77	364.6				0.537	1.065	2.538	0.022	1.98	4.73
41	495.8				0.543					
81	701.9				0.534	1.083	2.483	0.11	2.03	4.65
26	69.45	Ar	75.11	42.02	0.568					

c) Krypton Discharge Table IV presents the data using the krypton discharge. The values roughly parallel the xenon data.

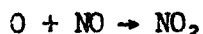
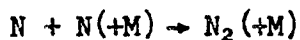
Table IV

Photolysis of Nitric Oxide; Krypton Discharge

Run No.	Initial NO (mmHg)	added gas	P (mmHg)	% NO	ϕ_{N_2}	ϕ_{NO_2}	ϕ_{NO}	N_2O	ϕ_{NO_2}/ϕ_{N_2}	ϕ_{NO}/ϕ_{N_2}
74	9.623				0.227	0.458	1.004		2.02	4.42
65	37.61				0.402	0.622	1.757	none	1.55	4.37
67	38.66				0.399	0.605	1.987		1.52	4.78
87	205.4				0.463	0.765	2.294	none	1.65	4.95
71	304.9				0.510	0.987	1.495		1.94	2.93
75	375.7				0.466	0.910	1.877		1.95	4.03
72	953.1				0.521	1.051			2.02	
73	10.24	N ₂	53.34	16.11		0.336	0.814			
88	158.4	Ar	384.6	29.06		1.194		none		
90	107.7	Ar	111.8	58.82		1.055				
85	10.45	Xe	48.52	17.70	0.340					

Discussion of Results

The data show that the quantum yield of N_2 production increases with increase in pressure of NO from 10 to 100 mm Hg. remaining approximately constant thereafter to higher pressures yielding a limit of about 0.5. The rate of yields of NO_2 to N_2 averages 2, while that for NO decomposed to N_2 produced in about 4. Since there is no marked increase in quantum yield as the available energy in the absorbed light is increased and the same limit 0.5 holds in each case, it seems certain that N_2 results from a recombination of nitrogen atoms. The quantum yield of NO_2 production approaches 1.0 as a limit at higher NO pressures indicating that only one oxygen atom is produced for each nitrogen atom. It is impossible to say whether NO_2 is produced by reaction of excess NO with O_2 formed by recombination of O atoms, which could occur even during the subsequent analysis, or from O and NO during the reaction period. Certainly the brown color of NO_2 is visible immediately the radiation is cut off. During the photolysis of 12 mm. NO using the hydrogen discharge a pressure decrease was observed which, assuming N_2 results from N atoms, suggests that O reacts with NO. The minimum significant reactions would be:-

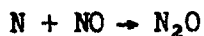


The energy of the krypton discharge can ionize NO:-



The similarity of the krypton data to those of hydrogen and xenon indicates that the ion-electron reaction produces an excited state which decomposes in a similar manner to the direct photolysis.

The production of N_2O probably occurs by the reaction:-



but further investigation of this is in progress as also of the effect of added inert gases.